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ANNUAL REPORT
for
DARPA/ONR
HIGH TEMPERATURE SUPERCONDUCTIVITY
PERIOD ENDING : June 30, 1989

I. PROGRAM INFORMATION

Contract Number:	N00014-88-C-0760
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Report Date	June 30, 1989

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II. PROGRAM SUMMARY

The overall goals of this program are to develop the technology of MBE growth of HTSC material, to optimize the performance of HTSC films with high transition temperatures and critical current densities, and to explore the development of electronic devices based on such material.

III. PROGRAM STATUS

We have obtained in-situ growth of $(BiO)_2$-containing HTSC material. We are attempting to perfect the process in order to improve the superconducting properties of the films.

IV ACCOMPLISHMENTS

Most notably, we have obtained $(BiO)_2$-containing layered superconducting films grown in-situ at low temperature without any post-growth anneal. This result was obtained recently on two films grown under nominally identical conditions using ozone as a source of active oxygen. To our knowledge, these are the first films from the $(BiO)_2$ family grown in-situ by an evaporative technique, and the first such films grown in-situ by any technique in the U.S.. The films were grown on $SiTiO_3$ by atomic layer epitaxy (ALE) and exhibited a streaky RHEED pattern throughout growth, indicating the heteroepitaxy of a single-crystal-like and atomically smooth layer. X-ray diffraction analysis revealed the films to be completely aligned, as layered by the beam-shuttering sequence, and nearly single phase. A very small amount of minority phase material was observed; it was also epitaxial. This represents an important step in the development of growth technology of HTSC compound thin films. With the perfection of the process, as discussed below, interesting multilayer structures should be obtained with atomically smooth and precise heterointerfaces. These include both device structures and novel material multilayerings.

The films exhibited almost identical resistivity versus temperature characteristics, with metallic behavior starting at around 500-1000 $\mu\Omega$-cm and showing the onset of a resistive transition above 50K followed by a sharp drop to zero at ~12K. This is shown in Fig. 1. Most of the film would seem to switch to being superconducting at the same temperature, giving a sharp transition

and indicating homogeneous material. The low transition temperature could be due to one of three factors. First, it may be that even though the film appears single-crystal-like and single-phase in its x-ray characteristics, it is conceivable that improper atomic layering could lead to reduced transition temperatures. Indeed, since only two films were grown before source problems forced a system shutdown, it is difficult to rule this out. A second possibility is that the ozone source is not able to oxidize the grown film adequately to give sufficient hole concentration for high transition temperatures. Finally, it is possible that the relatively thin samples, ~650 Å, suffered from substrate interaction that poisoned the films. A systematic study of a number of films varying the calibration coefficients in the vicinity of those determined by RBS analysis and varying the thickness of the films should clarify the situation.

The growth of superconducting films directly resulted from the use of a new ozone source for reactive oxygen and the use of an improved beam flux measurement and calibration scheme involving Rutherford backscattering (RBS) analysis. The ozone source is a generator/distillation system similar to that recently reported by the University of Minnesota. In our case, however, we use a silica gel charge to accumulate and store the O_3. A system of pumps and valves allows the stored volume to be further refined due to the differential vapor pressure between O_2 and O_3. The beam is introduced into the chamber through a water-cooled line. Only teflon, aluminum and stainless steel parts are used throughout the system to reduce surface catalyzed dissociation. The residual chamber gas can be analyzed with a quadrupole mass spectrometer. This shows the beam to be at least 33% ozone, which is almost an order of magnitude over the concentration of ozone out of the ozone generator itself. Films of CuO were grown at 600°C on MgO substrates over a range of oxidant mass flows. Even at a mass flow 1/10 that used to obtain growth of superconducting films, CuO and not Cu_2O grew. This is a substantial improvement in oxidation capability over the magnetron source previously used which exclusively gave insufficiently oxidized Cu_2O growth.

The new beam flux calibration and control scheme involves an improved beam pressure ionization gauge as well as the use of RBS to characterize absolute deposition rates. In order to obtain more precise and reproducible beam flux measurements using the in-situ ionization gauge, a collimator was introduced around the gauge

filaments to protect them from inadvertent coating during growth of films. This results in more constant metallurgical surfaces on the ionizer filament, the grid as well as the collector. By using a standard gauge conditioning protocol, similar to what is used to obtain good ion gauge measurements in III-V MBE, very reproducible beam flux measurements have been obtained. In the absence of beam flux drift, measurements over a six-hour period have routinely been constant to within less than 2%. This has allowed precise kinetic control of the deposited structure.

In order to obtain accurate calibration coefficients that relate ionization gauge reading to absolute beam flux, for example, in units of number/cm^2-sec, thin films grown at the desired substrate temperature using the target ozone flux have been grown by atomic layer epitaxy on MgO substrates. The layers are less than 1000 Å thick, which is convenient for RBS analysis. Since the substrate includes only atoms of lower atomic number, for sufficiently thin films each element is resolved into a separate peak. The integrated peak area for each of the elements, Bi, Sr, Ca and Cu, is then compared with the MgO substrate height which provides a standard. This results in measurements of the absolute flux for each source with error bars of less than 2%. The combined uncertainty of the RBS and beam flux measurements gives a total error bar of ~4% in the resulting calibration coefficients characterizing a given growth and system condition. Actual results on several calibration films show even less scatter in the data.

With such constant and well-characterized kinetic control, several films of highly metastable layering in the $(BiO)_2$-containing family of compounds have been grown. They were deposited using the old oxygen source, and as a result were not superconducting as grown; rather, they were semiconducting. They were, however, single-crystal-like and epitaxial as well as being atomically smooth. Figure 2 shows the x-ray diffraction patterns from a film layered to be the 2245 structure. The top curve is rocked 5° off the $SrTiO_3$ substrate in omega, while the lower curve is rocked off by 5° in omega. The main peaks can all be indexed to a 50.4 Å unit cell. In other films, we have seen surface-mediated, epitaxial-phase separation tending to favor the (2,2,n, n+1) Bi-Sr-Ca-Cu-O phases. Not surprisingly, these structures appear to be local minima in the configuration free energy at the growth temperature and oxygen flux used.

V PROBLEM AREA

The problem area currently is the relatively low transition temperature obtained to date from the in-situ $(BiO)_2$-containing HTSC films.

VI CORRECTIVE ACTION

We will continue to study source calibration and beam flux measurement reproducibility. We will also be studying the use of various applicators in supplying ozone to the growing surface. Attempts will be made to discover what is responsible for the low transition temperature obtained on the first two films.

VII GOALS FOR NEXT REPORTING PERIOD

1. To improve operation of ozone source and characterize its capabilities.

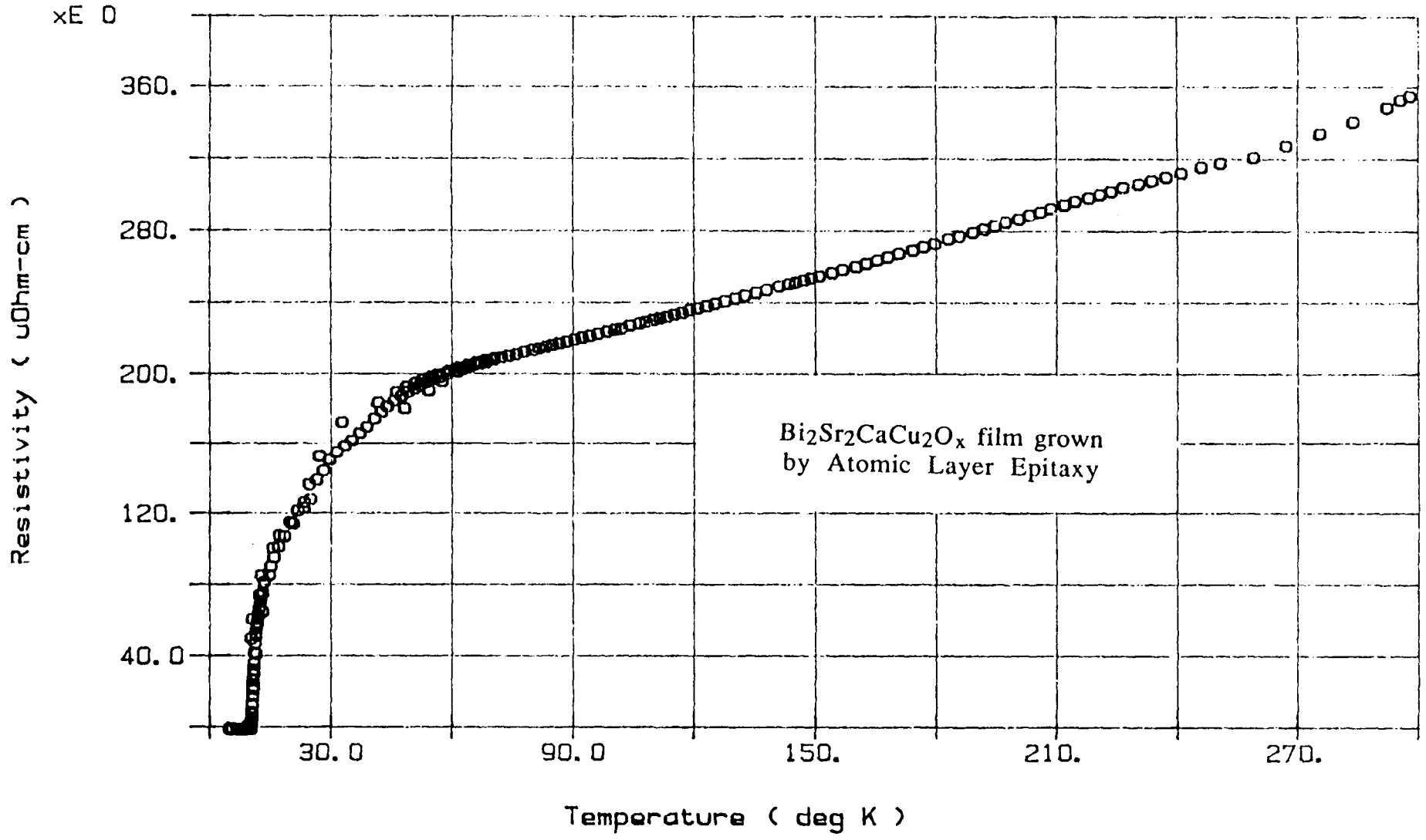
2. To continue examining RBS-based source calibration and to evaluate its consistency.

3. To grow improved atomically layered BiO-containing superconducting films, including metastable structures.

VIII FINANCIAL STATUS

Authorized funding to date:	$854K
Spending to date:	$200K plus ~$100K to be charged to Stanford subcontract when negotiated.
Funding required for fiscal year:	$340K

FIGURE 1

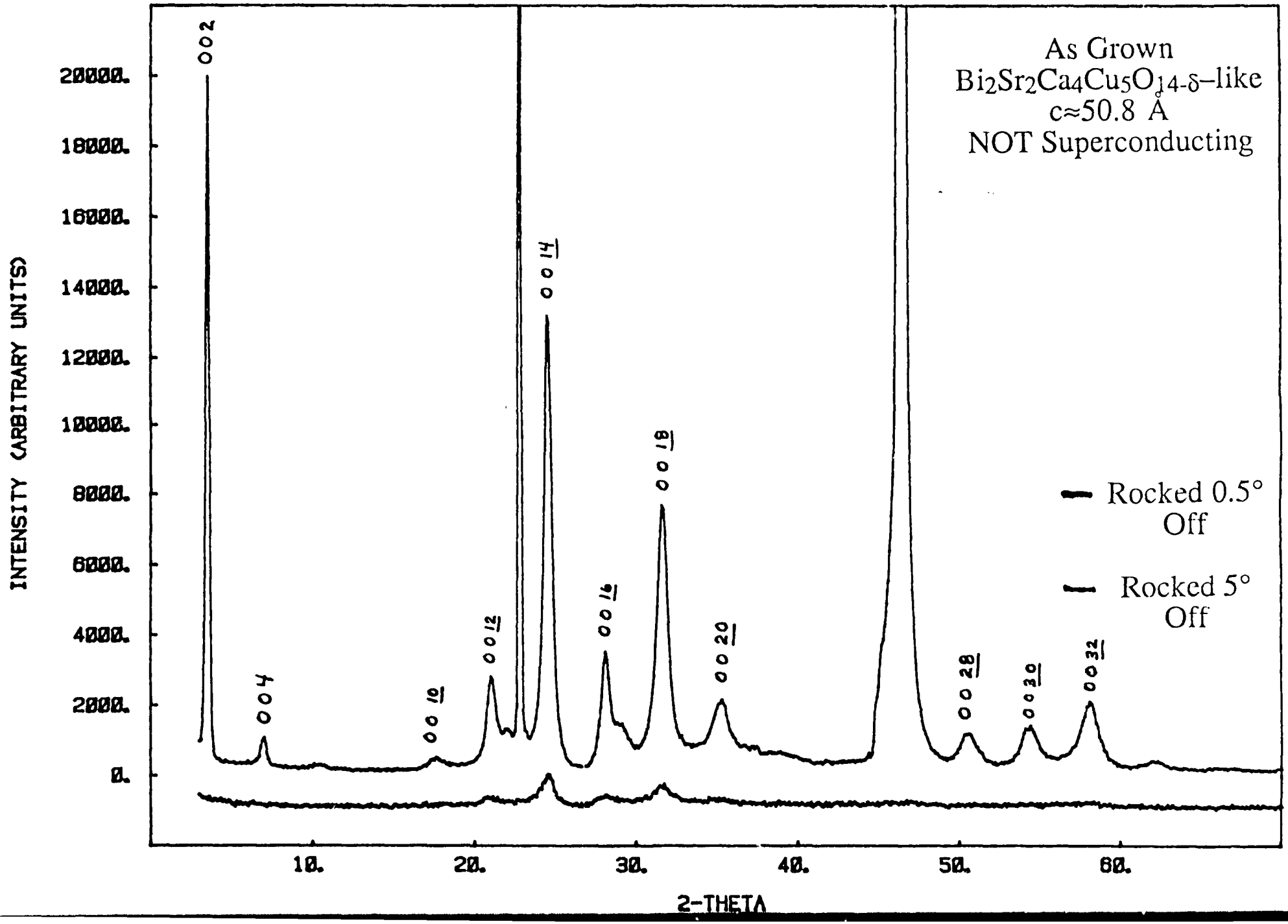


SAMPLE# : Bi252.RT1

DATE : 06/03/89

POINTS : 215

FIGURE 2


As Grown
Bi2Sr2Ca4Cu5O14-δ–like
c≈50.8 Å
NOT Superconducting
Rocked 0.5° Off
Rocked 5° Off
INTENSITY (ARBITRARY UNITS)
2-THETA
20000.
18000.
16000.
14000.
12000.
10000.
8000.
6000.
4000.
2000.
0.
10.
20.
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60.
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